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Magnetic properties of B2-structure CoZr upon ball milling

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Abstract

Magnetization measurements of B2-structure CoZr after high-energy ball milling have been performed at 4.2 K in the Amsterdam High Field Installation in fields up to 35 T. It turns out that the magnetic behavior of the ball-milled CoZr is drastically different from the unmilled sample. The magnetization at 21 T increases abruptly in the early state of milling due to the introduction of anti-site disorder in the B2-lattice. Upon amorphization the magnetization decreases. The magnetization of both the disordered crystalline compound and the amorphous material is not saturated up to 35 T. AC magnetic susceptibility and DC low-field magnetization measurements show that both disordered crystalline and amorphous CoZr exhibit a magnetic transition from the paramagnetic to the spin-glass-like state upon cooling with ordering temperatures of about 35 and 11 K, respectively, whereas the perfectly ordered (unmilled) compound is a paramagnet down to 4.2 K.

1. Introduction

In the past decade, an enormous amount of work has been performed on the mechanical milling in a high-energy ball mill. The reason is that it is very effective non-equilibrium processing technique to synthesize various metastable materials. So far, two types of ball milling experiments have been carried out, namely mechanical milling and mechanical alloying. Mechanical milling (MM) was termed for the milling process starting from ordered crystalline intermetallic compounds and mechanical alloying (MA) for the process starting from crystalline elemental powder mixtures. By MA and/or MM, various metastable materials have been obtained such as amorphous materials [1], crystalline phases existing in the phase diagram at high temperatures [2], solid solutions of immiscible systems [3], nanocrystalline materials [4] and quasicrystalline materials [5]. However, most of the work has been focused on the structural changes and

the underlying mechanisms. Little attention has been paid to the properties of these new materials. In previous studies [6–12] we demonstrated that besides other techniques magnetic measurements are unique to monitor the milling process of an intermetallic compound. The degree of (chemical) atomic disorder and phase transformation after milling of a compound can be determined by the observed change of magnetic properties e.g. saturation magnetization and magnetic ordering temperature. On the one hand, magnetic measurements are a sensitive probe to monitor structural changes of a compound. On the other hand, milling may induce materials with special magnetic properties because of the special induced atomic arrangements. This was recently observed in Co₂Ge and GdAl₂. Both ordered Co₂Ge and GdAl₂ are ferromagnets at lower temperatures. After milling, Co₂Ge eventually transforms to the amorphous state, while GdAl₂ disorders atomically but remains crystalline. It turned out that both amorphous Co₂Ge and atomically disordered crystalline GdAl₂ take a spin-glass state at low temperatures [13, 14]. In this way two novel *binary concentrated* spin-glass alloys were synthesized

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by mechanical milling. This inspired us to study the magnetic properties of various novel metastable phases. In this paper, we report on the study of magnetic properties of B2-structure CoZr upon mechanical milling.

2. Experimental results and discussion

For the experimental procedures the reader is referred to Refs. [11, 12].

It was derived from X-ray-diffraction patterns that the starting compound CoZr is single phase material crystallizing in the cubic B2-structure (ordered BCC). High-energy ball milling resulted in a decrease of the intensity and broadening of all Bragg peaks, indicating the introduction of atomic (chemical) disorder, internal stress and refinement of the crystallite size. The first amorphous trace was found in the material after 40 h of milling and the amorphization was complete after 160 h of milling. (The details of the structural development are presented elsewhere [15].) The lattice parameter turned out to increase by about 0.5%. These results suggest that anti-site atomic disorder occurs in CoZr during the early stage of milling. Eventually, after long periods of milling it induces amorphization.

High-field magnetization curves of CoZr at 4.2 K after various periods of milling are shown in Fig. 1. It is clear that both the magnetization and the magnetic susceptibility of the ball-milled CoZr are quite different from those of the starting compound. The value of the magnet-

ization of CoZr at 4.2 K increases strongly with milling time up to 40 h and decreases with further increasing milling time. It tends to become constant after 160 h of milling, where amorphization is completed. The magnetic susceptibility of the amorphous material is somewhat larger than that of the crystalline materials (both unmilled and milled for less than 40 h). Thus, the intersection of the two magnetization curves of the samples milled for 40 and 20 h also suggests that amorphization starts at a milling time of 40 h. The measured magnetization is an average of mixed crystalline and amorphous phases. It is interesting to note that magnetization of both the disordered crystalline compound (milled up to 20 h) and the amorphous material is not saturated up to 35 T. This indicates that the magnetic moments are rather randomly distributed in both materials.

The continuous increase of magnetization of CoZr with milling time is due to the rearrangement of Co and Zr atoms (atomic disorder) in the B2-lattice by milling. In the perfectly ordered B2-structure a Co atom is completely surrounded by non-magnetic Zr thereby losing its ferromagnetic character. In contrast, a Co atom on the 'wrong' sublattice (here on the Zr-sublattice) in the B2-lattice is surrounded by nearest-neighbor Co atoms, in this way forming a small cluster of cobalt metal. Thus anti-site Co atoms bear a magnetic moment and behave as ferromagnetic centers. The fact that the starting compound is almost non-magnetic (the curve 0 h) even at 4.2 K suggests that the as-prepared material is perfectly ordered i.e. both Co and Zr atoms occupy their own sublattices. Upon ball milling the magnetization of CoZr is increased largely, strongly indicating the generation of anti-site Co atoms. It was proposed in Ref. [15] that the type of disorder is anti-site disorder in CoZr. This means that both Co and Zr atoms are able to substitute sublattices of each other. Such an exchange certainly creates anti-site Co atoms and thereby magnetic centers. With increasing milling time the number of magnetic clusters will increase. Therefore, the average magnetization of CoZr increases continuously with milling time. However, upon amorphization the magnetization decreases again. This means that the short-range ordered state in the amorphous phase is different from that in the disordered crystalline compound. It is likely that the number of Co-Co nearest neighbors in the amorphous phase is less than in the disordered crystalline compound.

Fig. 2 shows the temperature dependence of the AC magnetic susceptibility χ_{AC} after milling for various periods. Upon cooling from room temperature to 4.2 K, no anomaly is detected in the starting compound (0 h). This means that the unmilled sample is a paramagnet from room temperature down to 4.2 K. However, upon mechanical milling the material becomes magnetically

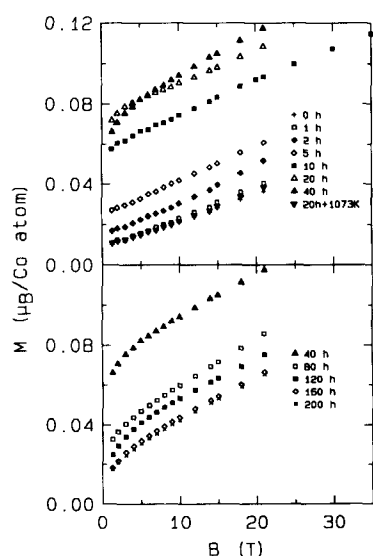


Fig. 1. High-field magnetization curves of CoZr at 4.2 K after various periods of milling.

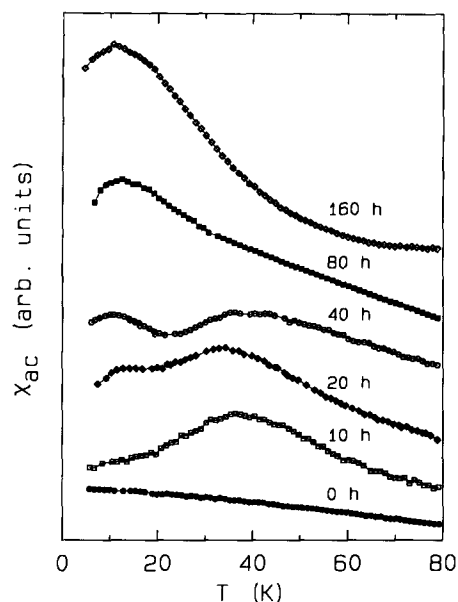


Fig. 2. Temperature dependence of the AC susceptibility χ_{AC} of CoZr after various periods of milling in an external AC field of 3 Oe and a frequency of 109 Hz.

ordered. After 10 h of milling a pronounced anomaly at about 35 K is observed. This is attributed to a magnetic ordering transition of the disordered crystalline CoZr. We call the corresponding peak 'peak-I'. The intensity of this transition increases upon further milling. After 20 h of milling another anomaly at about 11 K (peak-II) is visible. After 40 h of milling, the intensity of peak-I decreases somewhat while peak-II grows continuously. After 80 h of milling peak-I is not detectable any more but peak-II grows further. After 160 h of milling, peak-II becomes more pronounced and well-defined. Since the final product after 160 h of milling is amorphous CoZr, peak-II must be due to the magnetic ordering transition of amorphous CoZr. This anomaly already starts to occur in the sample after 20 h of milling. This means that amorphization in fact starts after 20 h of milling. The amorphous fraction in the sample after 20 h of milling is low so that the shape of the magnetization curve is not significantly influenced. Thus, AC susceptibility measurement provides more accurate information about the structural change of CoZr than X-ray diffraction because the values of the magnetic ordering temperature of the disordered crystalline on the one hand and amorphous phase on the other hand are quite different.

In order to better understand the nature of the magnetic ordering in these materials, the sample after 20 h of milling has been chosen for further study. The temper-

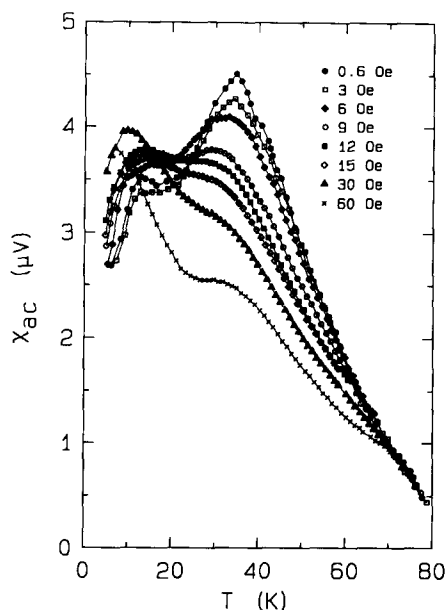


Fig. 3. Temperature dependence of the AC susceptibility χ_{AC} of CoZr milled for 20 h in various AC fields. A frequency of 109 Hz was used.

ature dependence of the AC magnetic susceptibility χ_{AC} in different AC fields is given in Fig. 3. Let us first inspect peak-I. It is seen that at low fields (< 6 Oe) a sharp asymmetric cusp occurs at 35 K which is defined as the transition temperature. When the field is raised the cusp disappears and only a broad maximum is found as illustrated for an applied field of 6 Oe in Fig. 3. At higher fields the maximum in χ_{AC} becomes more rounded and even a plateau. Both the transition temperature and the intensity decrease with increasing field. These phenomena are very similar to those observed by us in amorphous Co_2Ge [13] and disordered crystalline GdAl_2 [14] spin glasses and by Cannella and Mydosh for prototype spin glasses e.g. FeAu and MnCu [16, 17]. Now we proceed to peak-II. When a very small field e.g. 0.6 Oe is applied, a small cusp at about 11 K is observed. When a field of 3 Oe is applied, the transition intensity tends to decrease. Since this transition overlaps the low temperature part of peak-I, the transition shape and intensity are strongly dependent on those of peak-I. Therefore, the change of peak-II is unsystematic in the 'high-field' range. However, one point should be noted. That is, even in a field of 30 Oe, this transition still remains a peak-like maximum whereas peak-I already becomes rounded or only a plateau. This difference implies that the distribution of spin moments in the amorphous material is more random than that in the disordered crystalline compound.

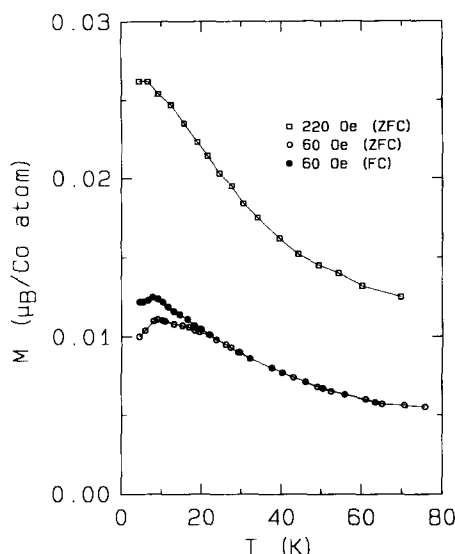


Fig. 4. Temperature dependence of the magnetization of CoZr milled for 20 h after zero-field cooling (ZFC) and field cooling (FC) in a field of 60 Oe. The ZFC curve measured in a field of 220 Oe is also included.

Low DC field magnetization measurements were used to confirm the results of AC susceptibility measurements. Thermal hysteresis of the magnetization below the ordering temperature, characteristic of a spin-glass is found. Fig. 4 gives the magnetization versus temperature curves of CoZr milled for 20 h after zero-field cooling (ZFC) and field cooling (FC) in a field of 60 Oe. The curve measured in a field of 220 Oe is also included. After ZFC and FC to 4.2 K measurements were successively made during heating. Let us inspect just the ZFC and FC curves in a field of 60 Oe. It is clear that both the ZFC and FC curves exhibit a maximum at about 9 K upon heating, which could be the ordering temperature of the amorphous phase in a field of 60 Oe. At higher temperature, there still exists a difference between the ZFC and FC curves. This is attributed to the irreversibility of the disordered crystalline phase. The two curves coincide at a temperature of about 21 K, the magnetic ordering temperature of the disordered crystalline phase. In a field of 220 Oe, only a gradual process is observed in the M versus T curve. This field is so high for both materials that the peak-like transition is smeared out.

From the above it is clear that the magnetic properties of atomically disordered crystalline and amorphous CoZr are characteristic of spin glasses. The originally ordered CoZr is a paramagnet down to 4.2 K. Upon milling, however, the material becomes two different spin-glass phases as a consequence of disorder on an atomic level. Thus the magnetic properties of the meta-

stable phases obtained by ball milling are markedly different from the stable forms. The spin-glass state which represents a metastable magnetic configuration of frozen-in disorder of the spin system adds another degree of disorder to a system which is already a disordered atomic array. The value of T_f of disordered crystalline CoZr is higher than that of amorphous CoZr. This means that the magnetic cluster sizes in disordered crystalline CoZr are on the average larger than those in amorphous CoZr. This is further reflected in the value of the magnetization.

3. Conclusions

Mechanical milling of paramagnetic CoZr compound resulted in two different spin-glass phases as a significant consequence of anti-site disorder in the B2-lattice and of induced amorphization. Both disordered crystalline CoZr and amorphous CoZr exhibit a transition from the paramagnetic to the spin-glass state at low temperatures with freezing temperature of 35 and 11 K, respectively. The freezing temperatures are lowered with increasing external field. Therefore, mechanical milling as a simple and easily controllable technique can be generally used to synthesize unusual and so far unknown interesting magnetic materials.

Acknowledgements

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